

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 194 375
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85307271.8

(51) Int. Cl.⁴: B 29 C 59/16

(22) Date of filing: 10.10.85

(30) Priority: 04.03.85 JP 42462/85
11.06.85 JP 126716/85
11.06.85 JP 126717/85

(43) Date of publication of application:
17.09.86 Bulletin 86/38

(84) Designated Contracting States:
DE FR GB IT NL

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(54) Method of crosslinking rubber and plastic moldings.

(57) A rubber or plastics molded article is made, e.g. by extrusion, containing a blowing agent and cross-linking agent, and is irradiated with electron beams, preferably from 2 (or 3) directions (Figures 1-3) at a low dose of not more than 50 Mrad and a voltage of not more than 3000kV to cross-link the surface layer only, the surface appearance and properties are thus preserved during subsequent steps.

The molding is then heated to complete the cross-linking and to cause foaming of the flowing agent to make an expanded (or cellular) product.

A separate cross-linkable surface layer can be provided by extrusion or coating.

Composite moldings, e.g. of expanded and unexpanded material, can be produced.

A continuous molding can be treated in a continuous process of extrusion, irradiation and foaming.

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METHOD OF CROSSLINKING RUBBER AND PLASTIC MOLDINGS

The present invention relates to a method of crosslinking the surface of a rubber or plastics molded article; and to a method of completing the production of such article.

5 Rubber and plastic expanded articles (hereinafter abbreviated to "expanded articles") are widely used, e.g. as automobile and bicycle parts, various industrial articles or building materials. For these uses, the expanded articles may be made of expanded materials alone
10 or combinations of expanded and unexpanded rubber and/or plastics, or combinations of such expanded materials and different materials such as metals. One important characteristic required for such expanded articles is that the expanded articles have good surface properties
15 and stable shape.

The surface properties of the expanded article referred to herein include not only properties concerning external appearance such as surface smoothness, luster, and vivid color but also mechanical properties such as
20 surface hardness, wear resistance, scratch resistance and low friction resistance, as well as chemical properties such as oil resistance and organic solvent resistance.

These properties are important for both expanded and unexpanded articles. In particular, they are important
25 when the article is in the expanded form (also called a sponge or cellular foamed article). In the case of such an expanded article, unevenness is liable to develop in the surface thereof during the production thereof, and so it is difficult to obtain a beautiful surface having
30 smoothness and luster. Also, if blowing agents or decomposition products thereof escape through the surface from the expanded molding during the process of expansion, water-absorbing resistance and wear resistance are lost and at the same time a soft feel cannot be obtained.

35 Another problem is that non-crosslinked rubber and plastic moldings cannot retain their desired forms

during the process of production thereof because of their own weight, deformation and distortion.

In the industrial production of a stabilized article surface, the production of expanded articles is more difficult than the production of unexpanded articles. This is considered to be due to the fact that the production of expanded articles requires additionally an unstable step of expansion.

The present invention seeks to overcome these problems.

The invention provides a method of crosslinking the surface of an expandable molded article made of a rubber or synthetic plastics material, which comprises irradiating the article with electron beams so as to cross-link its surface layer only. The invention also includes a method of completing the production of an expanded article which includes the step, following said irradiation, of heating the article to complete its cross-linking and cause its expansion.

The resultant molded articles of the invention have an improved appearance of their cross-linked surface layer.

The electrons beams are applied at a relatively low level, at a low dose and accelerated at a low electron voltage. Only the surface layer of the molding is thus limitedly crosslinked so that its inner portion is not crosslinked and is soft whereas its surface layer is hardened. This is important for the properties of the molding; the surface properties of the treated expanded article and its stable shape-retention are both greatly improved.

The nature of the moldings to be treated is not critical, provided that the rubber or plastic moldings is crosslinkable or has a crosslinkable surface layer.

When non-crosslinked compounds molded into a desired shape by extrusion molding, for example, are irradiated with electron beams, the surface layer thereof is hardened in such a condition that the shape and surface

properties obtained by the extrusion molding are retained in their original condition.

For example, when the surface of the non-cross-linked extrusion molding is very smooth, the surface is crosslinked while retaining its smoothness. When a cylindrical pipe is extruded from a die, the (non-cross-linked) molding which has just left the die is irradiated with electron beams, the surface of the pipe is hardened while retaining its original shape, and so deformation of the pipe is prevented.

Since expanded articles having a smooth surface are difficult to produce, it has been especially desired to develop a method of industrially producing expanded articles having improved surface properties.

This can be done by preliminarily molding cross-linkable rubber or plastic compositions containing a blowing agent by means of, e.g., an extruder, a calender roll, a roll or a press, and then heating the resulting moldings to thereby achieve the crosslinking and expansion with suitable timing.

However, if the crosslinking is carried out excessively in relation to the expansion, the expansion is attained only after the viscosity of the compound has increased and, therefore, it is difficult to obtain a high expansion rate (low density). Furthermore, the rate of crosslinking greatly varies with the kneading conditions of the expandable mixture, and also, the density of the expanded article varies with even a slight difference in heating conditions. Thus, it is difficult to retain stabilized shape and performance, and this leads to an increase in the level of defects amongst the articles produced. If the rate of crosslinking is low, the crosslinking and expansion can be well balanced with ease, and the number of defects can be reduced but with reduction in surface appearance.

Another important factor from an industrial standpoint is to produce the expanded articles having an expected performance and good surface appearance in high yield and with high productivity. Therefore in

conventional methods of producing expanded articles, it is necessary to control not only the rate of crosslinking (as in producing unexpanded articles) but also the rate of expansion, with high accuracy.

5 In the method of the invention, since the surface of a molding of a non-crosslinked composition containing a blowing agent and a crosslinking agent is irradiated with electron beams to form a crosslinked layer on its surface, and then crosslinking and expansion of the molding
10 are completed by heating, the surface of the expanded article can be made smooth regardless of the rates of crosslinking and expansion and the balance therebetween.

There are no special limitations on the method of preparing a non-crosslinked composition for making
15 an article treated by the present invention. As in conventional methods of the preparation of expanded rubber materials, such compositions can be prepared by kneading rubber material, resin, reinforcing filler, loading filler, softening agent, blowing agent, crosslinking agent, cross-
20 linking accelerator, stabilizer, and so forth by the use of a kneader such as a Banbury mixer, a kneader mixer, or a mixing roll.

Examples of starting material which can be used are rubbers and thermoplastic elastomers such as styrene-
25 butadiene rubber, polyisoprene rubber, polychloroprene rubber, acrylonitrile-butadiene rubber, polybutadiene rubber, ethylene-propylene rubber, ethylene-propylene-non-conjugated diene terpolymer rubber, acrylic rubber, natural rubber, polyethylene, chlorinated polyethylene,
30 an ethylene-vinyl acetate copolymer, or an ethylene- α -olefin copolymer, alone or in blends.

Typical examples of the blowing agent are dinitrosopentamethylenetetramine azodicarbonamide and p,p'-ortho-bisbenzenesulfonylhydrazine.

35 The means for crosslinking the rubber or plastic composition can be sulfur vulcanization, crosslinking using peroxides or crosslinking using quinoids.

The composition used can also contain usual additives such as a reinforcing filler, loading filler,

softening agent, crosslinking accelerator, coloring agent, stabilizer or antioxidant.

Such a non-crosslinked composition is formed into a desired shape by preliminary molding; any known techniques e.g. using an extruder, a calender roll, a press or a roll used.

In the conventional methods, such a molding is then transferred to the subsequent step of crosslinking and expansion without any additional treatment. But in the method of the invention the surface of the molding is irradiated with electron beams prior to the expansion, to form a crosslinked surface layer or skin layer.

In the irradiation, the optimum electron voltage and irradiation dose vary with the type of the starting material for the composition, the type of compounding ingredients, the compounding ratios, and so forth, and thus they can be determined appropriately by taking into consideration the above factors. The thickness of the crosslinked skin formed on the surface of the molding is influenced by the electron voltage of electron beams: as the electron voltage is increased, the thickness of the skin is increased.

The electron voltage is usually not more than 3,000 kV and preferably from 10 to 500 kV. The thickness of the skin layer formed at an electron voltage within the above range varies with the type of the composition; in general, the thickness is in the range of several microns to several hundred microns. If the electron voltage is too low, the thickness of the crosslinked skin layer is not sufficient. On the other hand, if the electron voltage is too high, the thickness of the crosslinked skin layer is excessive. In either case, a satisfactory rubber expanded article cannot be obtained.

The degree of crosslinking of the crosslinked skin layer varies with the dose of electron beams.

If this dose is too small, the skin layer cannot be sufficiently crosslinked, and the improvement of the surface appearance is small. On the other hand, if the

irradiation is too great, the crosslinking proceeds excessively and the strength of the skin layer is increased, whereby expansion is often prevented in the skin layer. The dose of electron beams irradiated in the present invention is usually not more than 50 Mrad and preferably from 1 to 30 Mrad.

After the crosslinked skin layer has been formed on the surface of the molding by irradiation with electron beams, the crosslinking and expansion of the molding are completed by heating.

For the crosslinking and expansion, conventionally used heating apparatus can be used. For example, a hot press, a hot air oven, a molten salt medium, a fluidized bed medium, a high frequency appliance, a steam pipe, and other heating units can be used; two or more heating systems can be used together.

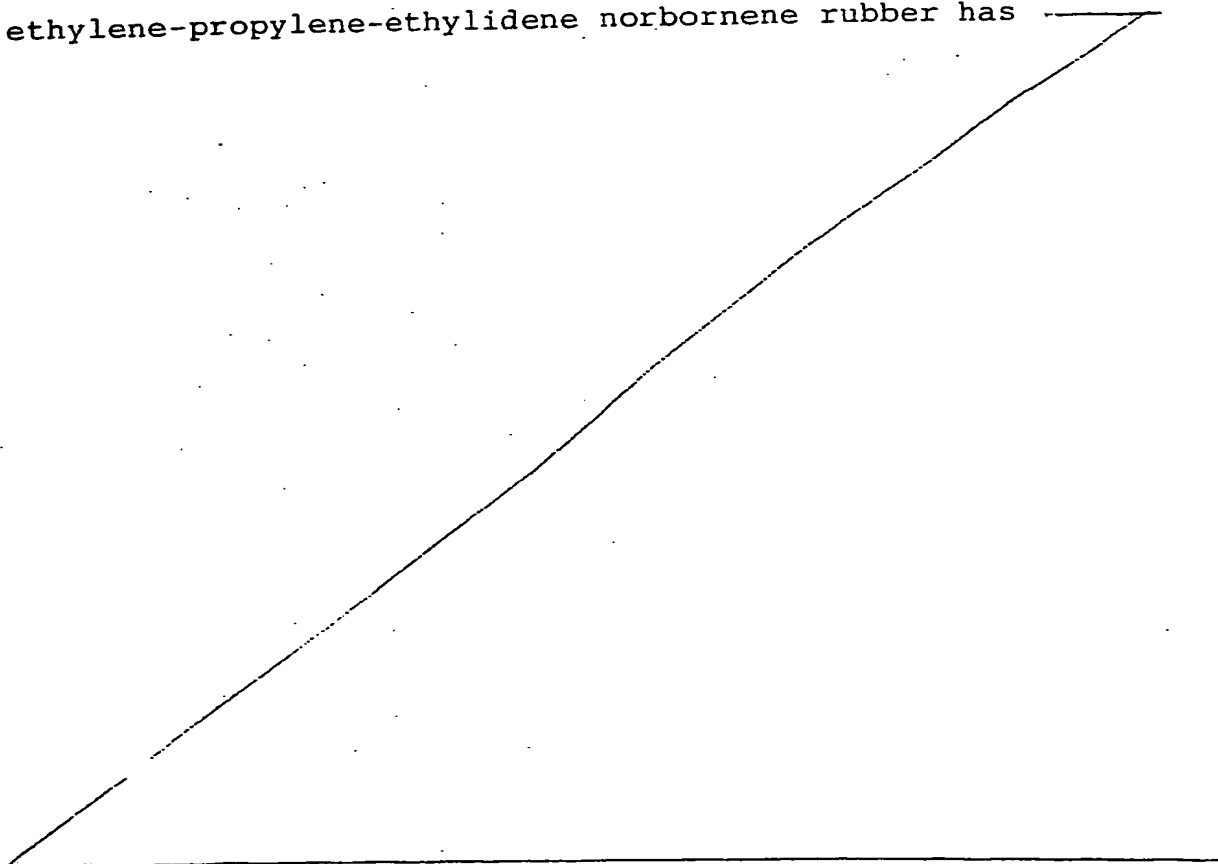
The heating temperatures for the crosslinking and expansion are the crosslinking temperature and the expansion temperature or higher, respectively, and they are chosen appropriately depending on the conditions employed.

An industrially important application of the present invention is the production of expanded rubber articles and composite articles.

If the method of the present invention is applied to an unvulcanized rubber composition having a rate of vulcanization smaller than the conventionally used rate of vulcanization, an expanded rubber article having a good surface appearance can be obtained. Accordingly, during the process of the production of expanded rubber articles, a difference in density can be decreased, and the number of defective articles can be reduced. Moreover, since the crosslinked layer is formed in the surface prior to the decomposition of the blowing agent, the flow of decomposed gases of the blowing agent through the surface can be markedly decreased. Thus an expanded rubber article having a lower density can be produced using the same amount of the blowing agent.

In one embodiment of the invention an expanded article having a good surface appearance can be produced using a non-crosslinked rubber composition having a low rate of vulcanization, which has hitherto been considered unsuitable for being expanded. This feature will hereinafter be explained in more detail.

One application is the production of an expanded article using an ethylene- α -olefin-dicyclopentadiene rubber. For example, the rate of vulcanization of an ethylene-propylene-dicyclopentadiene rubber is smaller than that of an ethylene-propylene-ethylidene norbornene rubber. Accordingly, in the conventional method wherein in order to produce a good surface condition, the rate of vulcanization must be higher than that of expansion, ethylene-propylene-ethylidene norbornene rubber has



exclusively been used. However, if the method of the present invention is applied, a satisfactory expanded article can be produced even by using the ethylene-propylene-dicyclopentadiene rubber as the starting material, without any problems.

Further, it has been found that the effect of the present invention can be applied for general purposes. That is, in the conventional methods of the production of expanded rubber articles, it has been considered to be required to set up the rate of vulcanization at a high level, depending on the rate of decomposition of the blowing agent. For this reason, as a composition for expanded article, a composition having a short scorch time, which is an index of an initiation time of vulcanization, has been considered suitable. In particular, in the case of producing the expanded article by continuous vulcanization or with vulcanizer, in order to make the surface of the expanded article smooth and to eliminate the formation of pin holes due to the release of gases, it is necessary to shorten the scorch time. For this reason, an expanded rubber composition containing an ethylene- α -olefin-non-conjugated diene rubber having a scorch time at 125°C of less than 5 minutes has been used. However, if the scorch time is shorter, the storage stability and the processing stability during the kneading

The method of the present invention solves the above contradiction. That is, in accordance with the present invention, a molding of a non-crosslinked rubber composition having a scorch time of 5 minutes or more is irradiated with electron beams and then heated, to thereby achieve the vulcanization and expansion, so that a rubber molding having an improved surface appearance can be produced without any problems of storage and processing stabilities. As the starting material, the above-described ones can be used. Other examples are rubber compositions having a relatively low rate of vulcanization, such as an ethylene- α -olefin-non-conjugated diene rubber and other rubbers, or mixtures of such rubbers and resins.

The method of the invention of uniformly irradiating the surface layer of rubber or plastic moldings with electron beams can be applied to a molding produced by extrusion. An improved _____

method of preliminary crosslinking of the extrusion molding is to uniformly irradiate the surface of such molding having a complicated shape with electron beams.

5 This uniform irradiation of the surface with electron beams is necessary for the following two reasons. One is to make the surface appearance uniform, and the other is to maintain original shape without deformation. Since electron beams go straight like light, when a molding having a circular cross-section is irradiated with electron
10 beams, it is necessary to irradiate the outer periphery of the molding with electron beams as much as possible.

A method of bending electron beams by the use of a magnet has been devised. This method, however, needs large equipment. On the other hand, in the present
15 invention, only the surface layer is limitedly irradiated with electron beams, unlike electrical wires in which electron beams are irradiated so as to penetrate through the electric wire. Thus the above method using a magnet is unsuitable in the present invention.

20 We have found that, in order to improve the surface appearance of the expanded molding and to retain an extruded shape, by the use of simple equipment the irradiation with electron beams is preferably performed from at least two directions.

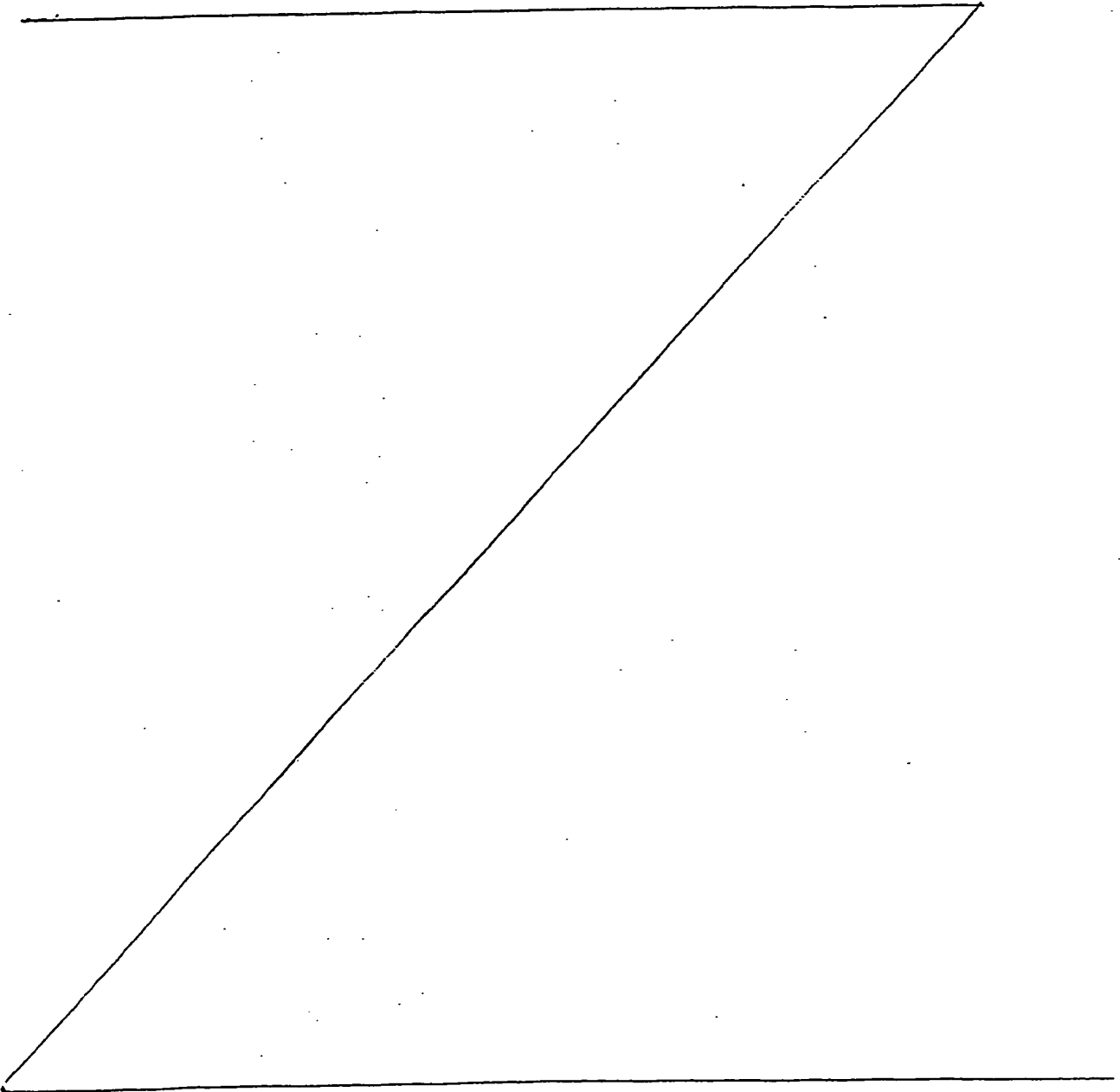
The method of the irradiation with electron
25 beams is illustrated in Figs. 1 to 4 wherein the reference 1 indicates a molding being irradiated with electron beams, 2 indicates the direction in which the irradiation with electron beams is applied, and indicates the angle of the irradiation.

30 Fig. 4 illustrates a case in which electron beams are irradiated onto the molding only from one direction. Figs. 1 to 3 illustrate the method of multi-directional irradiation, in which Fig. 1 illustrates a case in which electron beams are applied from two directions, and Figs. 2 and 3 illustrate cases of three-directional
35 irradiation.

The method shown in Fig. 3 is suitable for irradiation of the whole periphery of a molding having

a cylindrical, tube-like or complicated shape, whereby it is possible to irradiate the whole periphery if the effective irradiation width of an irradiated area is set up appropriately.

- 5 From the industrial and practical viewpoint, in many cases, the irradiation of the whole periphery with electron beams is not always required even for an



extrusion molding. when irradiation with electron beams is applied for the purpose of preliminarily crosslinking the surface layer so as to improve the smoothness, appearance or wear resistance of the surface, only the properties of a surface which can be seen or which comes into contact with other article is of importance. For example, in the case of a rubber expanded strip used in sealing of an automobile door, the properties such as appearance and wear strength of the surface area bonded to the automobile body can be often ignored. In this case, it suffices that, as illustrated in Fig. 1 or 2, the molding is partially irradiated with electron beams.

It is preferred that the irradiation with electron beams be applied from two or three directions. Particularly for a molding in which partial irradiation of one side is needed and which has a complicated shape, two-directional irradiation is preferred.

In such a case from the viewpoint of uniform irradiation, two-directional irradiation is sometimes superior to three-directional irradiation. The reason for this is considered to be because in the case of the three-directional irradiation, the degree of irradiation is partially high and, therefore, uniform

irradiation is rather prevented.

Advantages of the method shown in Fig. 1 in which the surface area of one side is partially irradiated with electron beams will become clear from the following
5 examples.

In the case of an extrusion molding, for example, it is preferred to employ a method in which electron beams are applied from two directions each at an angle of $45^\circ \pm 30^\circ$ from the axis extending upward in
10 relation to the horizontal plane passing through the center of the rubber and plastic molding (the angle α in Fig. 1 is $45^\circ \pm 30^\circ$).

The dose and electron voltage can be determined appropriately depending on the purposes. Since the object
15 of the present invention is to crosslink the surface layer, it can be attained by irradiation with electron beams in which the dose is relatively low and the electron voltage is relatively low.

The irradiation dose is suitably not more than 50 Mrad
20 and preferably from 1 to 30 Mrad. The electron voltage is suitably not more than 3,000 kV and preferably from 10 to 500 kV. Within these ranges, satisfactory crosslinking can be achieved.

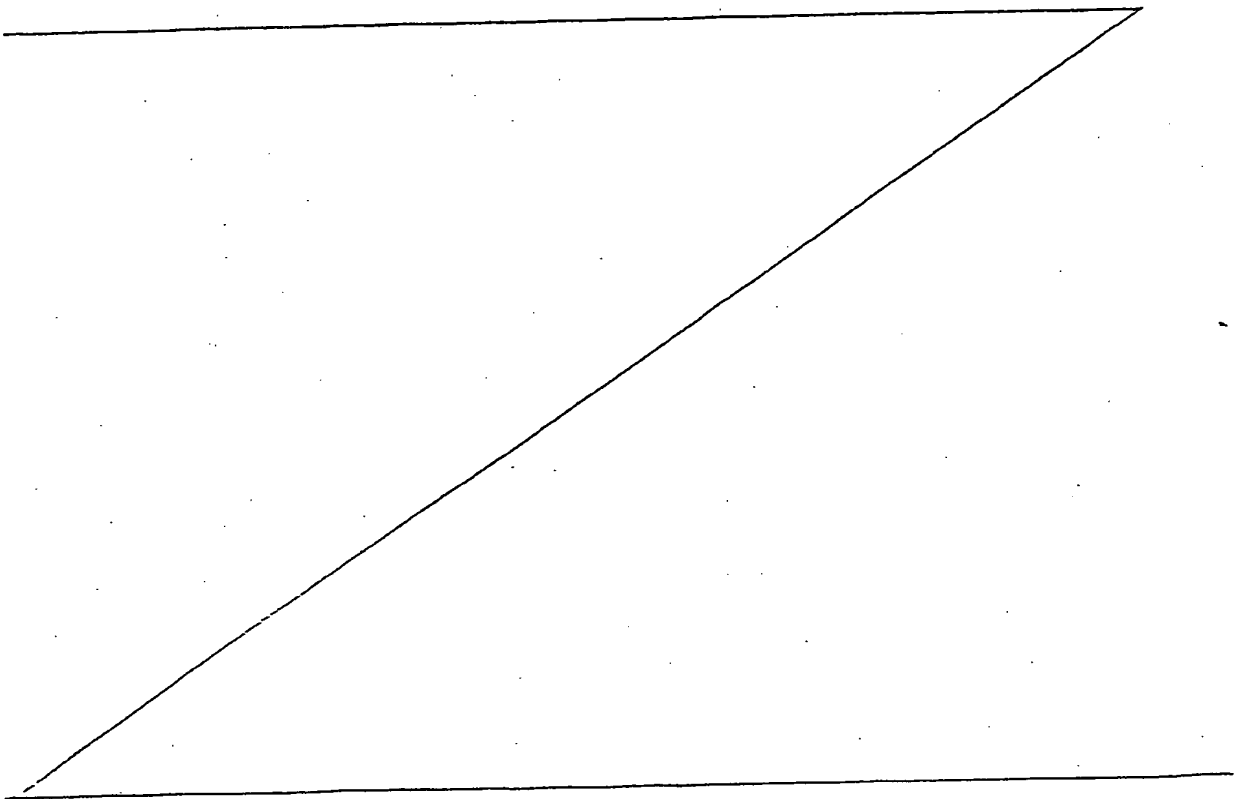
Although an extrusion molding that is produced
25 by continuous processing is suitable for use in the method

of the present invention, the invention is not limited thereto and can be utilized in continuous or batchwise irradiation of moldings produced by various methods.

Expanded rubber and plastic articles which can be produced effectively by the method of the present invention include an expanded material of rubber, a composite material of expanded rubber and unexpanded rubber, a composite of expanded rubber, unexpanded material and a metal, and an expanded rubber material covered with a plastics surface or expanded plastics material.

The molding to be irradiated can have a thin surface layer comprising a crosslinkable component, formed e.g. by coextrusion method or coating.

By selecting a suitable surface layer material,



characteristics such as excellent smoothness, luster, appearance, surface hardness, wear resistance, scratch resistance, low friction resistance, oil resistance, and organic solvent resistance can be imparted to the surface of the molding. Thus the ultimate product is increased in practical value.

The material forming a crosslinkable surface layer can be, for example, an unsaturated polyester resin, a urethane resin, an epoxy resin, an acrylic resin, a urethane-acrylic resin, a melamine-acrylic resin, an acrylated polyester resin or an epoxy-acrylic resin, alone or in combination.

There can be further incorporated therein coloring materials such as pigments and dyes, fillers, and additives. When it is necessary to crosslink also the inner layer portion, this is carried out before or after the crosslinking of the crosslinkable surface layer by irradiation with electron beams.

The present invention is described in detail with reference to the following examples.

EXAMPLES 1 TO 3 AND COMPARATIVE EXAMPLE 1

The effect of improvement in surface properties of an expanded article of an ethylene-propylene-ethylidene norbornene rubber according to the method of the present

invention is shown in these examples.

A composition shown in Table 1 was kneaded by the use of a Banbury mixer and a mixing roll to prepare an ethylene-propylene-ethylidene norbornene rubber composition for the preparation of an expanded article.

This rubber composition was extruded in the form of a tube through an extruder. After irradiation of the surface of the extrudate with electron beams, the extrudate was heated at 230°C for 5 minutes in a hot air oven to conduct vulcanization and expansion, whereupon an expanded rubber article was obtained.

TABLE 1

	<u>Formulation</u>	<u>Amount</u> (parts by weight)
	Esprene® 505 ^{*1}	100
	Zinc oxide	5
15	Stearic acid	1
	FEF carbon black	70
	Calcium carbonate	40
	Paraffin oil	40
	p,p-Oxybisbenzenesulfonyl- hydrazine	3
20	Soxinol® BZ ^{*2}	2.0
	Soxinol® TRA ^{*2}	1.0
	Soxinol® M ^{*2}	2.0
	Sulfur	1.5

Note:

*1 Ethylene-propylene-ethylidene norbornene rubber
(produced by Sumitomo Chemical Company, Limited)

*2 Vulcanization accelerator (produced by Sumitomo
5 Chemical Company, Limited)

The expanded article of the rubber was evaluated
for surface appearance. The results are shown in Table 2
along with its apparent specific gravity.

TABLE 2

	<u>Dose of Electron Beams Irradiated (Mrad)</u>	<u>Surface Appearance of the Expanded Article*2</u>	<u>Apparent Specific Gravity of the Expanded Article</u>
Comparative Example 1	-	C	0.522
10 Example 1	2	A	0.521
Example 2	5	A	0.519
Example 3	10	A	0.520

Note:

*1 Electron voltage: 250 kV

15 *2 The surface appearance of the expanded article
was rated as follows:

A : Excellent
B : Good
C : Fair

It can be seen from the results of Table 2 that irradiation with electron beams greatly improves the surface appearance of the expanded rubber article without any change of a degree of expansion. That is, the effect of the present invention is great.

EXAMPLE 4 AND COMPARATIVE EXAMPLE 2

A composition shown in Table 3 was kneaded by the use of a Banbury mixer and a mixing roll to prepare an ethylene-propylene-dicyclopentadiene rubber composition.

10 This rubber composition was extruded in the form of a tube by the use of a 45 mm ϕ extruder (die: 100°C). After irradiation of the surface of the extrudate with electron beams, the extrudate was heated at 230°C for 5 minutes in a hot air oven to achieve vulcanization and
15 expansion, whereupon an expanded article of the rubber was obtained.

TABLE 3

	<u>Formulation</u>	<u>Amount</u> (parts by weight)
	Esprene [®] 305 ^{*1}	100
	Zinc oxide	5
20	Stearic acid	1
	FEF carbon black	80
	Calcium carbonate	40
	Paraffin oil	40

	p,p-Oxybisbenzenesulfonyl- hydrazine	3
	Soxinol [®] BZ ^{*2}	1.5
	Soxinol [®] TRA ^{*2}	1.0
	Soxinol [®] M ^{*2}	1.0
5	Sulfur	1.5

Note:

*1 Ethylene-propylene-dicyclopentadiene rubber
(produced by Sumitomo Chemical Company, Limited)

*2 Vulcanization accelerator (produced by Sumitomo
10 Chemical Company, Limited)

The expanded article of the rubber was evaluated
for surface appearance. The results are shown in Table 4
along with its apparent specific gravity.

TABLE 4

	<u>Dose of Electron Beams Irradiated (Mrad)</u>	<u>Surface Appearance of the Expanded Article^{*2}</u>	<u>Apparent Specific Gravity of the Expanded Article</u>
Example 4	5	A	0.47
15 Comparative Example 2	-	D	0.56

Note:

*1 Electron voltage: 200 kV

*2 The surface appearance of the expanded article
was rated as follows:

A : Excellent
B : Good
C : Fair
D : Poor

5 It can be seen from the results of Table 4 that a sponge having a good surface appearance, a high degree of expansion, and a low apparent specific gravity which has been considered to be impossible to produce from an ethylene-propylene-dicyclopentadiene rubber can be easily
10 produced by applying the method of the present invention.

EXAMPLES 5 TO 8 AND COMPARATIVE EXAMPLES 3 TO 6

In these examples, blends of an ethylene-propylene-dicyclopentadiene rubber and an ethylene-propylene-ethylidene norbornene rubber were used.

15

TABLE 5

Formulation	Amount (parts by weight)
Ethylene-propylene-dicyclopentadiene rubber*1	} 100
Ethylene-propylene-ethylidene-norbornene rubber*2	
Zinc oxide	5
20 Stearic acid	1
FEF carbon black	100
Calcium carbonate	40
Paraffin oil	55

	p,p-Oxybisbenzenesulfonyl- hydrazine	3
	Soxinol [®] BZ ^{*3}	1.5
	Soxinol [®] TE ^{*3}	0.7
	Soxinol [®] M ^{*3}	2.0
5	Sulfur	1.5

Note:

- *1 Ethylene-propylene-dicyclopentadiene rubber
(Mooney viscosity, $ML_{1+4}(100^{\circ}C)$: 70, propylene content:
35 wt%, iodine value: 20)
- 10 *2 Ethylene-propylene-ethylidene norbornene rubber
(Mooney viscosity, $ML_{1+4}(100^{\circ}C)$: 73, propylene content:
40 wt%, iodine value: 20)
- *3 Vulcanization accelerator (produced by Sumitomo
Chemical Company, Limited)
- 15 The composition shown in Table 5 was kneaded in
the same manner as in Example 1 and then extruded through
a 45 mm ϕ extruder using a Garbay die at a die temperature
of 100°C. The extrudate was irradiated with electron
20 beams in the same manner as in Example 1 and then
vulcanized and expanded in a hot air oven.

The results obtained are shown in Table 6.

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TABLE 6

	Comparative Example 3	Example 5	Comparative Example 4	Example 6	Comparative Example 5	Example 7	Comparative Example 6	Comparative Example 8
Dicyclopentadiene- based EPDM	100		70	30			0	
Ethylidene norbornene-based EPDM	0		30	70			100	
Compound Mooney Viscosity ML ₁₊₄ (100°C)	42		42	44			45	
Scorch Time, t ₅ at 125°C (min)* ₁	7.7		5.8	3.5			3.1	
Dose of Electron Beams (Mrad)* ₂	-	5	-	5	-	5	-	5
Sponge Characteristics								
Surface Appearance	D	A	D	A	B	A	B	A
State of the Edge Portion* ₃	B	B	B	B	C	C	D	D
Apparent Specific Gravity	0.57	0.48	0.54	0.51	0.54	0.53	0.56	0.56

Note: *1 Scorch Time: Measured by JIS K6301.

*2 Electron Voltage: 200 kV.

*3 Evaluation of extrusion properties using a Garbay die was rated as follows.

A : Excellent

B : Good

C : Fair

D : Poor

It can be seen from the results of Table 6 that when an ethylene-propylene-dicyclopentadiene rubber is irradiated with electron beams, a sponge product having good extrusion properties and surface appearance can be obtained.

In the case that an ethylene-propylene-ethylidene norbornene rubber is used, since its scorch is short, the surface appearance is good even if it is not irradiated with electron beams, but the scorch phenomenon occurs during the process of extrusion and the composition can not be extruded uniformly.

EXAMPLE 9 AND COMPARATIVE EXAMPLES 7 TO 9

A composition shown in Table 7 was kneaded by the use of a Banbury mixer and a mixing roll to prepare a sponge composition comprising an ethylene-propylene-ethylidene norbornene rubber.

TABLE 7

<u>Formulation</u>		<u>Composition (A)</u> (part by weight)	<u>Composition (B)</u> (part by weight)
Esprene® 502*1		100	100
20 Zinc oxide		5	5
Stearic Acid		1	1
FEF carbon black		80	80
Calcium carbonate		40	40
Paraffin Oil		60	50

	p,p-Oxybisbenzenesulfonyl- hydrazine	3	3
	Soxinol [®] BZ*2	1.5	1.0
	Soxinol [®] TRA*2	1.0	0.5
	Soxinol [®] M*2	1.5	1.0
5	Sulfur	1.5	1.5
<hr/>			
	Compound Scorch Time, t ₅ at 125°C (min)	3.6	6.2

Note:

*1 Ethylene-propylene-ethylidene norbornene rubber
(produced by Sumitomo Chemical Company, Limited)

10 *2 Vulcanization accelerator (produced by
Sumitomo Chemical Company, Limited)

This sponge composition was extruded in the form
of a tube by the use of a 45 mmØ extruder (tube
die: 80°C).

15 The surface of the extrudate thus obtained was
irradiated with electron beams. Then the extrudate was
heated at 230°C for 5 minutes in a hot air oven to achieve
vulcanization and expansion, whereupon a tube-shaped
sponge was obtained. The sponge thus obtained was
20 evaluated for surface appearance, apparent
specific gravity and extrusion molding stability. The
results are shown in Table 8.

TABLE 8

	Compara- tive <u>Example 7</u>	Compara- tive <u>Example 8</u>	Compara- tive <u>Example 9</u>	<u>Example 9</u>
Composition	(A)	(A)	(B)	(B)
Dose of Electron Beams Irradiated*1 (Mrad)	-	5	-	5
Surface Appearance of Expanded Article*2	B	A	C	A
Apparent Specific Gravity of Expanded Article	0.50	0.51	0.54	0.51
5 Extrusion Stability*2	C	C	A	A

Note:

*1 Electron voltage: 200 kV

*2 The surface appearance and molding properties
were rated as follows:

10 A : Excellent

B : Good

C : Poor

It can be seen from the results of Table 8 that
in the composition B having a long scorch time and good
15 molding stability, if electron beams are applied, the
surface appearance of the sponge can be greatly improved.
In the case of the composition (A) having a short scorch
time, even if electron beams are not applied, a sponge

having relatively good surface appearance can be obtained, but the scorch phenomenon occurs and molding stability is poor.

EXAMPLES 10 TO 12 AND COMPARATIVE EXAMPLE 10

5 In these examples, it is shown that if electron beams are applied from a plurality of directions, the effect of excellent shape-sustaining properties can be obtained.

10 A composition shown in Table 9 was kneaded by the use of a Banbury mixer and a mixing roll for the preparation of an expanded article.

15 This rubber composition was extruded in the form of a tube by the use of an extruder. After irradiation of the surface of the extrudate with electron beams, the extrudate was heated at 230°C for 5 minutes in a hot air oven to accomplish vulcanization and expansion, whereupon an expanded article of the rubber was obtained.

20 The irradiation with electron beams was applied in three different manners: from one direction, from two directions, and from three directions as shown in Figs. 4, 1, and 2, respectively. In each of the manners, the electron voltage was 250 kV, and the dose of electron beams irradiated was 10 Mrad.

25 Each expanded article was evaluated, and the results are shown in Table 10.

It can be understood from the results of Table 10 that the surface appearance can be improved without substantial change in the apparent specific gravity of the expanded article by irradiation with electron beams. In connection with the shape-retaining properties, irradiation from the two directions (Fig. 1) and the three directions (Fig. 2) is effective.

TABLE 9

	<u>Formulation</u>	<u>Amount</u> (parts by weight)
10	Esprene [®] 502 ^{*1}	100
	Zinc oxide #3	5
	Stearic acid	1
	FEF carbon black	80
	Calcium carbonate	40
15	Paraffin oil	40
	p,p-Oxybenzenesulfonylhydrazine	3
	Sulfur	1.5
	Soxinol [®] BZ ^{*2}	1.5
	Soxinol [®] TRA ^{*2}	1.0
20	Soxinol [®] M ^{*2}	1.5

Note:

*1 Ethylene-propylene-ethylidene norbornene rubber
(produced by Sumitomo Chemical Company, Limited)

*2 Vulcanization accelerator (produced by Sumitomo

Chemical Company, Limited)

TABLE 10

	Comparative Example 10	Example		
		10	11	12
Irradiation Manner	No irradiation	One direction (Fig. 4)	Two directions (Fig. 1 $\alpha=45^\circ$)	Three directions (Fig. 2)
5 Irradiation Dose (Mrad)	-	10	10	10
Electron Voltage (kV)	-	250	250	250
Expanded Article of Rubber				
Surface Appearance*1	C	B	A	A
Apparent Specific Gravity	0.50	0.48	0.48	0.48
10 Shape-Retention Ratio*2(%)	76	63	95	87

Note:

*1 The surface appearance of the expanded article was rated as follows:

- 15 A : Excellent
 B : Good
 C : Poor

*2 Shape-retention ratio

20 This is indicated by a ratio of the outer diameter (d_1) in the vertical direction of the tube to the outer diameter (d_2) in the horizontal direction of the tube: $(d_1/d_2) \times 100(\%)$. As the ratio is nearer 100%, the properties are better.

CLAIMS:

1. A method of cross-linking the surface of an expandable molded article made of a rubber or a synthetic plastics material, characterised by irradiating the article with electron beams so as to crosslink its surface layer only.

2. A method as claimed in Claim 1, wherein the irradiation with electron beams is carried out at a dose of not more than 50 Mrad and at an electron voltage of not more than 3,000 kV.

10 3. A method as claimed in Claim 1 or 2, wherein the surface of the molding was previously provided with a surface layer composed of a crosslinkable component.

4. A method as claimed in Claim 1, 2 or 3, wherein the surface layer of the molding is uniformly crosslinked by irradiating the molding with electron beams from at least two directions.

15 5. A method as claimed in Claim 1, 2 or 3, wherein the molding is a non-crosslinked molding containing at least one of a natural rubber and a synthetic rubber or polyolefin-based resin as a major component.

20 6. A method as claimed in Claim 1, 2 or 3, wherein the molding is composed of one or more of an ethylene- α -olefin rubber, a styrene-butadiene rubber, a polychloroprene rubber, an acrylonitrile-butadiene rubber, an polyisoprene rubber, a polybutadiene rubber, a chlorinated polyethylene and a chlorosulfonated polyethylene.

25 7. A method as claimed in Claim 1, 2 or 3, wherein the rubber or plastic molding is a molding composed of a thermoplastic elastomer.

30 8. A method as claimed in Claim 1, 2 or 3 wherein the molding is a non-crosslinked rubber molding containing an ethylene- α -olefin-non-conjugated diene rubber.

9. A method as claimed in Claim 1, 2 or 3, wherein the molding is a non-crosslinked rubber molding composed mainly of a synthetic rubber and having a scorch time at 125°C of at least 5 minutes.

5 10. A method of producing an expanded rubber or plastics molding from an article which has been surface crosslinked by a method as claimed in any preceding claim, the molding containing a blowing agent, which is characterised by heating the article to complete the cross-linking
10 and to cause expansion of the blowing agent.

11. A method as claimed in Claim 11, wherein the molding also contains a crosslinking agent, and after the irradiation the crosslinking with the crosslinking agent and expansion with the blowing agent are carried
15 out.

12. A method as claimed in Claim 10 or 11, wherein the molding is a continuously molded product, and the molding of the rubber or plastic composition, the irradiation with electron beams and the subsequent
20 steps are carried out continuously.

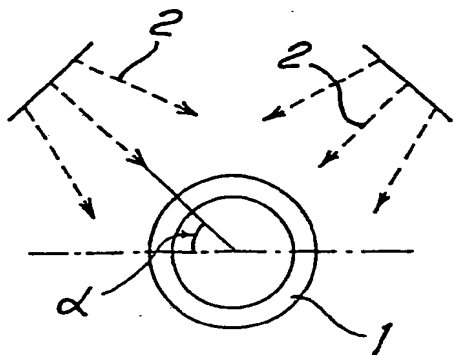


FIG. 1

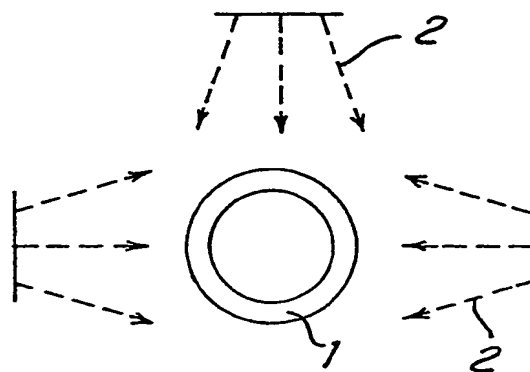


FIG. 2

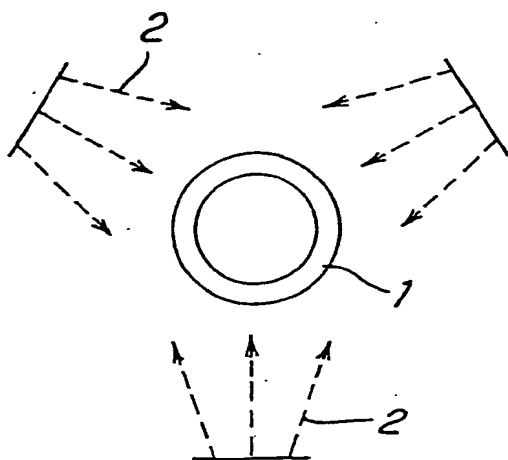


FIG. 3

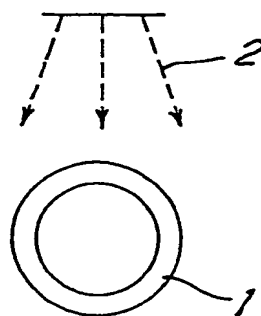


FIG. 4

12 **EUROPEAN PATENT APPLICATION**

21 Application number: 85307271.8

51 Int. Cl.³: B 29 C 59/16

22 Date of filing: 10.10.85

30 Priority: 04.03.85 JP 42462/85
11.06.85 JP 126716/85
11.06.85 JP 126717/85

43 Date of publication of application:
17.09.86 Bulletin 86/38

88 Date of deferred publication of search report: 16.03.88

84 Designated Contracting States:
DE FR GB IT NL

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54 **Method of crosslinking rubber and plastic moldings.**

57 A rubber or plastics molded article is made, e.g. by extrusion, containing a blowing agent and cross-linking agent, and is irradiated with electron beams, preferably from 2 (or 3) directions (Figs 1-3) at a low dose of not more than 50 Mrad and a voltage of not more than 3000kV to cross-link the surface layer only, the surface appearance and properties are thus preserved during subsequent steps.

The molding is then heated to complete the cross-linking and to cause foaming of the blowing agent to make an expanded (or cellular) product.

A separate cross-linkable surface layer can be provided by extrusion or coating.

Composite moldings, e.g. of expanded and unexpanded material, can be produced.

A continuous molding can be treated in a continuous process of extrusion, irradiation and foaming.

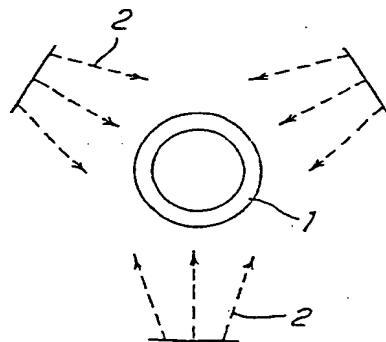


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

0194375

Application Number

EP 85 30 7271

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 207, 13th September 1983, page 113 M 242; & JP-A-58 104 726 (AISHIN SEIKI K.K.) 22-06-1983 * Abstract; patent publication, page 2, left-hand column, lines 5-16 *	1-3,5,7 ,10-12	B 29 C 59/16
E	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 123, 8th May 1986, page 74 C 344; & JP-A-60 248 747 (SUMITOMO KAGAKU KOGYO K.K.) 09-12-1985 * Abstract; patent publication, page 2, right-hand column, upper corner, lines 15-20 *	1,2,5-11	
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 122, 26th May 1983, page 122 C 168; & JP-A-58 42 630 (NITTO DENKI KOGYO K.K.) 12-03-1983 * Abstract *	1-3,5-11	
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 46, 27th February 1985, page 24 M 360; & JP-A-59 184 629 (SEKISUI KAGAKU KOGYO K.K.) 20-10-1984 * Abstract *	1-7,10,11	TECHNICAL FIELDS SEARCHED (Int. Cl.4) B 29 C
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-12-1987	Examiner LABEEUW R.C.A.
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	